

---

# Decoupling Approximations for Quantum Vibrational Predissociation Dynamics: Tests on the Low-Level Golden Rule Approaches for Some Rare Gas—Cl<sub>2</sub>, ICl Complexes

---

A. A. BUCHACHENKO,\* A. YU. BAISOGOLOV, and N. F. STEPANOV

*Laboratory of Molecular Structure and Quantum Mechanics, Department of Chemistry, Moscow State University, Moscow 119899, Russia*

*Received 12 January 1995; accepted 3 July 1995*

---

## ABSTRACT

Vibrational and rotational decoupling approximations are tested in three-dimensional Fermi Golden Rule calculations on energies, lifetimes, and product state distributions of the vibrationally predissociating atom–diatom van der Waals complexes. The validity of approximate separations of diatom vibration, decoupling of stretching and bending intermolecular motions, and rotational infinite order sudden approximation for product scattering is characterized by comparison with the results of accurate calculations on the Ne ⋯ Cl<sub>2</sub>, Ne ⋯ ICl, and He ⋯ ICl systems. The most accurate approximate schemes are recommended. © 1996 by John Wiley & Sons, Inc.

---

## Introduction

**D**uring the past two decades, considerable attention has been paid to decay processes in weakly bound molecular complexes, in particular the vibrational predissociation (see, for example, refs. 1 and 2). The increasing ability of experimental techniques to gain accurate state-resolved characteristics of metastable complexes has stimu-

lated the rapid progress in complementary theoretical approaches. Nowadays the quantum dynamics problem of vibrational predissociation (VP) for an atom–diatom system is successfully solved at the (numerically) exact level in time-independent<sup>3</sup> and time-dependent<sup>4</sup> formalisms.

However, approximate quantum approaches are interesting for several reasons. The main reason corresponds to potential energy surface (PES) determination. VP processes are often observed for the electronically excited complexes whose PESs are not usually well defined. At the same time, for

\* Author to whom all correspondence should be addressed.

many systems VP rates and product state distributions constitute the substantial and most reliable part of experimental information reflecting the structure of the PES. Therefore, one should explore potential inversion procedures based on the VP observables (the first examples of this approach may be found in ref. 5). Requiring large-scale dynamical calculations, they must employ simple and cheap computational schemes. Analysis of various approximations for "half-collision" predissociation dynamics also seems interesting, opening, first, perspectives for studying more complex systems and allowing, second, detection of useful parallels with the well-developed methods of inelastic scattering theory.<sup>6</sup>

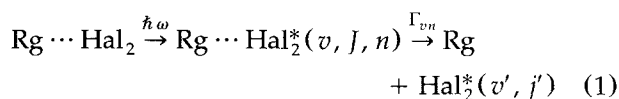
In this article we resorted to the simplest (low-level) approximations for the time-independent Fermi Golden Rule (FGR) treatment of three-dimensional VP dynamics of the atom-diatom complexes possessing zero total angular momentum. Detailed comparison with results of the benchmark calculations on the  $\text{Ne} \cdots \text{Cl}_2$ ,  $\text{Ne} \cdots \text{ICl}$ , and  $\text{He} \cdots \text{ICl}$  complexes permitted us to estimate the validity of the approximations for different dynamical quantities and formulate practically useful recipes for their applications.

In the next section we describe the relevant dynamical approximations. Then we present numerical results for the reference systems. Finally, we discuss our findings and present conclusions.

## Theory

### VIBRATIONAL PREDISSOCIATION

Vibrational predissociation of a van der Waals (vdW) complex is a rupture of a weak intermolecular bond induced by energy transfer from a vibrationally excited molecular fragment. For the particular case of rare gas-halogen molecule complexes, this process can be described as<sup>1c</sup>



where the star indicates the electronically excited halogen fragment;  $v, v'$  are its initial and final vibrational quantum numbers;  $n$  denotes the vibrational excitation of vdW degrees of freedom;  $J$  is the total angular momentum of the complex; and  $j'$  is the rotational quantum number of the product halogen molecule. Equation (1) corresponds to the optical pumping of metastable state

$(v, n)$ , which then decays into  $(v', j')$  channels ( $v' < v$ ) with a definite rate, or predissociation width  $\Gamma_{vn}$ .

VP dynamics is conveniently treated using Jacobi coordinates  $r$ ,  $R$ , and  $\vartheta$  ( $r$  denotes internuclear  $\text{Hal}_2$  separation,  $R$  is the distance between the diatom center of mass and Rg atom, and  $\vartheta$  is the angle between  $R$  and  $r$  vectors). The total Hamiltonian of the complex has the form<sup>1c</sup>

$$H = -\frac{1}{2m} \frac{\partial^2}{\partial r^2} - \frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\mathbf{j}^2}{2mr^2} + \frac{\mathbf{l}^2}{2\mu R^2} + U_{\text{mol}}(r) + U_{\text{int}}(r, R, \vartheta) \quad (2)$$

Here  $m$ ,  $\mu$  are the relevant reduced masses, and  $\mathbf{j}$  and  $\mathbf{l}$  are the rotational and orbital angular momentum operators. The potential energy surface consists of two parts  $U_{\text{mol}}$  and  $U_{\text{int}}$  representing intra- and intermolecular interactions, respectively.

### FERMI GOLDEN RULE APPROACH

Two general features of the weakly bound systems—namely, the smallness of intermolecular interaction with respect to the molecular vibrational level spacing and the large mismatch in the classical frequencies of intra- and intermolecular motions (adiabatic invariance)—strongly support the validity of perturbative treatment of predissociating complexes.<sup>1c</sup> That is, the total Hamiltonian [eq. (2)] may be expanded as

$$H = H_0 + V \quad (3)$$

where the unperturbed Hamiltonian  $H_0$  describes the uncoupled intra- and intermolecular subsystems

$$H_0 = h_{\text{mol}} + h_{\text{int}} \quad (4)$$

and the perturbation operator  $V$  containing the coupling terms is small enough. Hence, to zero order, metastable states of  $H$  correspond to the bound states of  $H_0$ ,

$$H_0 \Psi_{vn}^0 = E_{vn}^0 \Psi_{vn}^0 \quad (5)$$

and their widths can be evaluated in the first order as coupling matrix elements with the isoenergetic continuum states<sup>3,7</sup>

$$\Gamma_{vn} = 2\pi |\langle \Psi_E | V | \Psi_{vn}^0 \rangle|^2 \delta(E - E_{vn}^0) \quad (6)$$

where  $\Psi_E$  is the continuum eigefunction of the total Hamiltonian  $H$  at energy  $E$ .

### Bound State Problem

To evaluate bound state wave function  $\Psi_{vn}^0$ , a recipe for construction of the unperturbed Hamiltonian [eq. (4)] should be adopted. Conveniently, its intramolecular part is represented by the isolated molecular oscillator<sup>1c</sup>

$$h_{\text{mol}} = -\frac{1}{2m} \frac{\partial^2}{\partial r^2} + U_{\text{mol}}(r) \quad (7)$$

which defines the vibrational functions  $\chi_v$

$$h_{\text{mol}} \chi_v(r) = \varepsilon_v \chi_v(r) \quad (8)$$

The intermolecular Hamiltonian acquires the form

$$h_{\text{int}} = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \tilde{B}j^2 + \frac{1^2}{2\mu R^2} + \tilde{U}_{\text{int}}(R, \vartheta) \quad (9)$$

where  $\tilde{B}$  and  $\tilde{U}_{\text{int}}$  are the effective diatomic rotational constant and interaction potential in which the dependence on  $r$  is eliminated. This may be done within two basic approximations. The first one is vibrational diagonal adiabatic decoupling (VDA), which keeps the  $r$  coordinate fixed at some point  $\bar{r}$ . The simplest choice implemented in early studies on VP dynamics<sup>8</sup> is  $\bar{r} = r_e$ , the equilibrium distance of diatom. Since the derivative couplings are neglected in  $H_0$ , we use the term VDA. The effective rotational constant and potential in eq. (9) are therefore

$$\tilde{B} = 1/2mr_e^2 \equiv B_e; \quad \tilde{U}_{\text{int}}(R, \vartheta) = U_{\text{int}}(r_e; R, \vartheta) \quad (10)$$

We designated this equation as VDA- $r_e$ . A slightly improved VDA approximation (VDA- $r_v$ ) may be obtained by setting  $\bar{r} = r_v = \langle \chi_v | r | \chi_v \rangle$ , the vibrationally averaged diatomic internuclear separation. Then

$$\tilde{B} = 1/2mr_v^2; \quad \tilde{U}_{\text{int}}(R, \vartheta) = U_{\text{int}}(r_v; R, \vartheta) \quad (11)$$

so that the intermolecular Hamiltonian becomes dependent on vibrational excitation of the diatomic fragment.

The vibrational diabatic decoupling (VDD) scheme commonly used in accurate VP dynamics calculations<sup>3</sup> is analogous to the Born-Oppenheimer approximation for the "fast" and

"slow" vibrational subsystems. It implies that slow motions are controlled by the Hamiltonian averaged over the "fast" variables.<sup>1c</sup> That is,

$$\tilde{B} = \frac{1}{2m} \langle \chi_v | r^{-2} | \chi_v \rangle \equiv B_v; \quad \tilde{U}_{\text{int}}(R, \vartheta) = \langle \chi_v | U_{\text{int}}(r, R, \vartheta) | \chi_v \rangle_r \quad (12)$$

The Schrödinger equation

$$h_{\text{int}} \Phi_n(R, \vartheta) = E_n \Phi_n(R, \vartheta) \quad (13)$$

for the bound van der Waals levels may be solved either variationally or by invoking the diabatic decoupling approximation for radial and angular motions, as suggested in ref. 9. In the latter approach, one seeks for  $\Phi_n$  in the form

$$\Phi_n(R, \vartheta) = \phi_{n_s}(R; \vartheta) F_{n_b}(\vartheta) \quad (14)$$

where the radial function  $\phi$  depends on the angle parametrically and therefore is not subjected to the action of angular momentum operators. It can be found from the solution of the one-dimensional radial equation

$$\left[ -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \tilde{U}_{\text{int}}(R; \vartheta) \right] \phi_{n_s}(R; \vartheta) = W_{n_s}(\vartheta) \phi_{n_s}(R; \vartheta) \quad (15)$$

at a series of angle values. The corresponding eigenvalues  $W$  determine the effective potential for the angular Schrodinger equation<sup>9b</sup>

$$\left[ \frac{1}{4\mu} \{1^2, \langle \phi_{n_s} | R^{-2} | \phi_{n_s} \rangle\} + \tilde{B}j^2 + W_{n_s}(\vartheta) \right] F_{n_b}(\vartheta) = E_{n_s, n_b} F_{n_b}(\vartheta) \quad (16)$$

where the term in braces is the anticommutator of two angular-dependent operators. It is convenient to expand  $F_{n_b}$  over the rigid rotor basis functions, which, in the special case of zero total angular momentum  $\mathbf{J} = \mathbf{1} + \mathbf{j} = 0$ , are simply the spherical harmonics  $Y_{k0}$ :

$$F_{n_b} = \sum_k a_k^{(n_b)} Y_{k0} \quad (17)$$

The  $n_s$  and  $n_b$  indexes in the preceding equations mean the approximate vdW stretching and bending quantum numbers corresponding to the single good quantum number  $n$  [eq. (13)] and  $E_{n_s, n_b}$  [eq. (16)] approximate  $E_n$  in eq. (13). This procedure for evaluating quasibound wave functions

will be referred to as the fixed angle approximation (FAA).

A variational solution of eq. (13) implies the expansion of  $\Phi_n$  over appropriate radial and angular bases  $\mathcal{R}_p(R)$ ,  $\Theta_q(\vartheta)$

$$\Phi_n = \sum_p \sum_q C_{pq}^{(n)} \mathcal{R}_p \Theta_q \quad (18)$$

where  $\Theta_q$  may be chosen as a linear combination of  $Y_{k0}$

$$\Theta_q = \sum_k b_k^{(q)} Y_{k0} \quad (19)$$

if  $J = 0$ .

### Product Scattering Problem

In principle, in the rigorous FGR approach [eq. (6)],  $\Psi_E$  should be determined from a system of close-coupled equations for interacting continua orthogonal to the initial bound state, or open product scattering channels  $(v', j')$ .<sup>3</sup> However, it does not formally suffer from considering various decoupling approximations. In what follows we will deal with a family of the simplest methods, which completely uncouple vibrational and rotational channels.

The separation of intramolecular motion in the scattering problem coincides with that implemented earlier for bound state calculations. Namely, the  $\Psi_E$  function in eq. (6) is replaced by  $\Psi_E^0$ , the continuum state function of the unperturbed Hamiltonian  $H_0$ , which corresponds to a definite asymptotic channel:

$$\Psi_E^0 = \Psi_{v'j'\varepsilon}^0 = \chi_{v'}(r) \Phi_{j'\varepsilon}(R, \vartheta) \quad (20)$$

Here  $\varepsilon$  is the translational energy release and  $\Phi_{j'\varepsilon}$  is the eigenfunction of  $h_{\text{int}}$  which, as before, may be constructed within the VDA- $r_e$ , VDA- $r_v$ , or VDD schemes.

The fixed angle approximation for scattering wave function is equivalent to the celebrated rotational infinite order sudden approximation (RIOSA)<sup>6</sup>:

$$\Phi_{j'\varepsilon}(R, \vartheta) = \phi_\varepsilon(R; \vartheta) Y_{j'0}(\vartheta) \quad (21)$$

where  $\phi_\varepsilon$  is the solution of the following radial equation at frozen angle  $\vartheta$ :

$$\left[ -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \tilde{B}j(\tilde{j} + 1) + \frac{\tilde{l}(\tilde{l} + 1)}{2\mu R^2} + \tilde{U}_{\text{int}}(R; \vartheta) \right] \cdot \phi_\varepsilon(R; \vartheta) = \varepsilon \phi_\varepsilon(R; \vartheta) \quad (22)$$

Here  $\tilde{l}$  and  $\tilde{j}$  define some fixed expectation values of the corresponding angular momentum operators.<sup>6</sup>

There is, however, an important point which distinguishes the RIOSA for inelastic scattering and VP problems. Indeed, in the former, substitution of the  $j^2$  operator by an effective expectation value under the energy sudden approximation merely fixes the rotational energy of diatom, so only the  $\tilde{l}$  parameter reflects the angular momentum of a scattering wave function. Hence,  $\tilde{l}$  should be assigned to some physically meaningful quantum number ( $J, l, l'$ , etc.) to ensure correct summation of partial waves into the cross section.<sup>6</sup> In the VP problem, the scattering wave function possesses unique and definite angular momentum and energy, so both  $\tilde{j}$  and  $\tilde{l}$  may be conveniently treated as true angular momentum expectation values.

Therefore, one can suggest the following parameterizations for RIOSA wave functions (note that  $J = 0$  constraint requires  $\tilde{l} = \tilde{j}$ ):

1.  $\tilde{l} = 0$ . This choice is equivalent to the  $\tilde{l} = J$  assignment of the scattering RIOS approximation and will be referred to as RIOSA- $J$ .
2.  $\tilde{l} = \langle l \rangle$ , where  $\langle l \rangle$  is determined from the average value of the  $l^2$  operator on the initial bound state wave function. This choice is evidently reminiscent of the scattering RIOSA parameterized by the initial value of orbital momentum (RIOSA- $l$ ).
3.  $\tilde{l} = l' = j'$ , the RIOSA- $l'$  counterpart.
4.  $\tilde{l} = (\langle l \rangle + l')/2$ , the analog of symmetrized  $(l + l')/2$  parameterization<sup>10</sup> denoted here as RIOSA- $l_{\text{av}}$ .

### Golden Rule Integrals

Within a completely decoupled approximation for the product scattering, the total predissociation width  $\Gamma_{vn}$  [eq. (6)] is expressed as an incoherent sum of partial widths

$$\begin{aligned} \Gamma_{vn} &= \sum_{v'j'} \Gamma_{vn \rightarrow v'j'} \\ &= 2\pi \sum_{v'j'} \left| \langle \chi_{v'}(r) \phi_{\varepsilon,j'}(R; \vartheta) Y_{j'0}(\vartheta) \right. \\ &\quad \left. \times |V| \chi_v(r) \Phi_n(R, \vartheta) \rangle \right|^2 \end{aligned} \quad (23)$$

where

$$\begin{aligned}\varepsilon_{v'j'} &= E_{v_n}^0 - \varepsilon_{v'} - \tilde{B}j'(j' + 1) \\ &= \varepsilon_v - \varepsilon_{v'} + E_n - \tilde{B}j'(j' + 1)\end{aligned}\quad (24)$$

$$V = U_{\text{int}} - \tilde{U}_{\text{int}} \quad (25)$$

and summation is performed over all open channels ( $\varepsilon_{v'j'} > 0$ ).

## Results

### Ne $\cdots$ Cl<sub>2</sub>. I

As the first example we chose the Ne $\cdots$ Cl<sub>2</sub> system whose dynamics were thoroughly studied by Halberstadt, Beswick, and Janda.<sup>3a</sup> For the PES which models the Ne—Cl<sub>2</sub>( $B^3\Pi(O_u^+)$ ) interaction, those authors obtained converged photodissociation cross sections near the lowest resonance ( $n = 0$ ) associated with  $v = 11$  excitation of the diatom and derived resonance position and width from the lineshape analysis. The diabatically decoupled FGR approximation combined with fully close-coupled scattering wave functions was also used by those authors. We tested the less rigorous approaches formulated earlier for the same model.

### Rotational Decoupling Approximations

Table I compares the data of ref. 3a with the results of various diabatically decoupled schemes (time-dependent result from ref. 4a obtained with

the same PES is also included for completeness). Our most exact VDD/RIOSA methods differ from the FGR approximation of Halberstadt et al.<sup>3a</sup> by the decoupling of rotational as well as vibrational scattering channels. However, the second factor seems not very important here since the two-quantum  $v' = 9$  channel contributes little to the total decay width. Thus, the discrepancy between our data and the literature data stems almost completely from the RIOSA.

Differently parameterized RIOS approximations give close lifetime values with the deviation from the reference value less than 8%. All versions of the RIOSA strongly overcool rotational product state distributions, although the RIOSA- $l'$  scheme performs better. Representative plots of rotational distributions obtained with the different computational approaches are shown in Figure 1.

Table I also demonstrates the performance of the FA approximation for bound state wave functions. This method works well for energy and, being combined with the RIOSA- $J$ ,  $l$ , or  $l'$  scattering wave functions, almost completely reproduces the widths calculated with variational bound state wave functions. The RIOSA- $l_{\text{av}}$  parameterization, however, strongly underestimates the lifetime and predicts qualitatively wrong rotational product state distribution peaked at  $j' = 0$  instead of  $j' = 2$  (see Fig. 1).

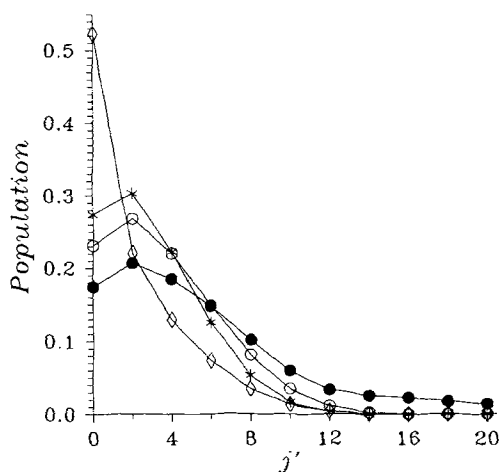
To summarize, the choice of angular momentum parameters strongly influences the results of RIOSA calculations of total and partial decay widths. We found that  $\bar{l} = l'$  parameterization is the best,  $\bar{l} = \langle l \rangle$  one provides the comparable ac-

**TABLE I.**  
Energy, Lifetime, and Product State Distributions for the Ne  $\cdots$  Cl<sub>2</sub> ( $v = 11$ ) Complex (Model I). Rotational Decoupling Approximations.

Method	Energy (cm <sup>-1</sup> )	Lifetime (ps)	$P_{v'=10}$ <sup>a</sup> (%)	$\langle E_{\text{rot}} \rangle$ <sup>b</sup> , cm <sup>-1</sup>	
				( $v' = 10$ )	( $v' = 9$ )
VDD FAA / RIOSA- $J$	-48.01	325	99.88	2.0	2.6
/RIOSA- $l$		298	99.88	2.0	2.6
/RIOSA- $l'$		274	99.87	2.7	3.9
/RIOSA- $l_{\text{av}}$		171	99.91	1.3	1.8
VDD / RIOSA- $J$	-47.68	324	99.84	1.9	3.2
/RIOSA- $l$		294	99.84	1.9	3.2
/RIOSA- $l'$		287	99.85	2.4	4.1
/RIOSA- $l_{\text{av}}$		299	99.83	2.2	3.8
VDD / VRCC <sup>3a</sup>	-47.70	300	99.87	7.4	9.3
Lineshape (ref. 3a)	-47.66	321	—	7.8	—
Wave packet (ref. 4a)	-47.59	300	—	—	—

<sup>a</sup>Percentage of population in  $v' = 10$  channel.

<sup>b</sup>Averaged rotational energies in the  $v' = 10$  and  $v' = 9$  channels.



**FIGURE 1.** Rotational distributions of dissociation products of the  $\text{Ne} \cdots \text{Cl}_2$  ( $B, v = 11$ ) complex (model I): filled circles — lineshape,<sup>3a</sup> stars — VDD FAA/RIOSAJ, open circles — VDD FAA/RIOSAJ', diamonds — VDD FAA/RIOSAJ'av.

curacy, and the standard choice  $\bar{l} = 0$  is not optimal. The RIOSA- $l_{av}$  scheme can be used only in combination with variational bound state wave functions. These conclusions are also confirmed by the analysis of the second  $n = 1$  resonance ( $n_s = 0$ ,  $n_b = 1$ ).<sup>3a</sup>

### Vibrational Decoupling Approximations

Table II presents the data obtained within the different vibrationally decoupled schemes for RIOSA- $l'$  scattering wave functions. The results for energy, lifetime, and vibrational branching ratios are systematically corrected along the VDA- $r_e$ , VDA- $r_v$ , and VDD sequence. The highest accuracy

of VDD approximation is evident. The VDA- $r_v$  approximation produces close results, markedly improving the VDA- $r_e$  approach. As should be expected, the latter scheme is the worst. However, the difference between VDA- $r_e$  and VDD lifetimes amounts to only 50%, but not the orders of magnitude, as in the two-dimensional case.<sup>11</sup> These trends do not depend on whether or not the FA approximation is invoked for bound state solution.

### Basis Sets for the Variational Method

We used the  $\text{Ne} \cdots \text{Cl}_2$  system also for analyzing the properties of several basis sets for variational solution of the bound state problem. Three types of radial bases  $\mathcal{R}(R)$  were tested. The first one consists of the harmonic oscillator functions, while the other two include numerical eigenfunctions evaluated for effective radial potential  $\tilde{U}_{\text{int}}(R; \vartheta)$  at the fixed equilibrium angle  $\vartheta$ . Since the shallow potential well usually supports only few bound states, we augmented this basis with numerical discretized continuum wave functions obtained by placing the infinite<sup>12a</sup> or finite<sup>12b</sup> wall far enough from the interaction region; the position and height of the wall were optimized in the test calculations. These functions were calculated using the efficient renormalized Numerov method based on a phase formalism.<sup>13</sup>

We have found that the infinite-wall discretized continuum basis yields slow convergence of variational solution, whereas the convergence rate of the finite-wall basis is slightly lower for the ground state and much higher for excited states than that of the harmonic basis (providing that the angular functions  $\Theta$  are the same).

**TABLE II.** Energy, Lifetime, and Product State Distributions for the  $\text{Ne} \cdots \text{Cl}_2$  ( $v = 11$ ) Complex (Model I). Vibrational Decoupling Approximations.

Method	Energy ( $\text{cm}^{-1}$ )	Lifetime (ps)	$P_{v'=10}$ <sup>a</sup> (%)	$\langle E_{\text{rot}} \rangle^b$ , $\text{cm}^{-1}$	
				( $v' = 10$ )	( $v' = 9$ )
VDA- $r_e$ FAA/RIOSAJ'	-49.28	386	99.87	3.1	4.3
VDA- $r_e$ /RIOSAJ'	-47.22	201	99.80	2.9	6.0
VDA- $r_v$ FAA/RIOSAJ'	-48.44	236	99.85	4.2	5.0
VDA- $r_v$ /RIOSAJ'	-48.11	275	99.84	2.9	3.4
VDD FAA/RIOSAJ'	-48.01	274	99.87	2.7	3.9
VDD/RIOSAJ'	-47.67	287	99.85	2.4	4.1
VDD/VRCC (ref. 3a)	-47.70	300	99.87	7.4	9.3
Lineshape (ref. 3a)	-47.66	321	—	7.8	—

<sup>a</sup>Percentage of population in  $v' = 10$  channel.

<sup>b</sup>Averaged rotational energies in the  $v' = 10$  and  $v' = 9$  channels.

For the angular basis we also explored two possibilities. In the first the coefficients  $b_k$  in eq. (19) were found by one-dimensional diagonalization of the effective angular Hamiltonian with the potential given by a section of  $\tilde{U}_{\text{int}}$  at equilibrium  $R$  value, while in the second the  $\Theta$  functions were taken as the  $F$  functions [eq. (17)]—that is, as the angular functions of the fixed angle approximation defined by eq. (16). The variational solution for the ground vdW state converges in the first basis somewhat faster, but the FAA basis exhibits by far more rapid convergence with respect to the total number of the bound states supported by the potential well and provides better description for levels with higher bending excitations.

Therefore, the numerical radial eigenbasis augmented by finite-wall discretized continuum functions in combination with the fixed-angle contraction scheme for the angular basis may be quite efficient for the problems requiring computations on the whole spectrum of vdW levels.

### Ne $\cdots$ Cl<sub>2</sub>. II

The Ne  $\cdots$  Cl<sub>2</sub> ( $B$ ) potential energy surface implemented in Ref. 3a and in the previous subsection does not provide quantitative agreement with the experimental data on this complex.<sup>14</sup> In ref. 15 another PES has been suggested and involved in the vibration-rotation close coupling FGR calculations (VDD/VRCC) on the positions and widths of  $n = 0$  resonances associated with  $v = 6, 9, 11$ , and 13. These data allow us to analyze the behavior of approximate computational schemes for different excitation energies of diatom.

Table III summarizes the results for resonance positions obtained within different vibrational decoupling approximations together with those taken from refs. 15 and 4a (note that most figures cited in ref. 15 were not explicitly given therein and were actually taken from ref. 4a). The VDD FAA approach underestimates the resonance energy (with respect to the variational solution) by ca.  $0.6 \text{ cm}^{-1}$ , and this difference only slightly increases with  $v$ . The results of VDA- $r_v$  approximation are very close to VDA- $r_e$  ones and exhibit very weak dependence on  $v$ . Evidently, the VDA- $r_e$  approach predicts the same resonance position for any excitation energy.

Table IV accumulates the data on lifetimes. The VDA- $r_e$  and VDA- $r_v$  estimations bound the VDD ones from above and below, respectively, and the relative deviations from the latter grow up with  $v$ .

**TABLE III.**  
Resonance Energies of the Ne  $\cdots$  Cl<sub>2</sub> Complex (Model II),  $\text{cm}^{-1}$ .

Method	$v = 6$	$v = 9$	$v = 11$	$v = 13$
VDA- $r_e$ FAA	−55.86	−55.86	−55.86	−55.86
VDA- $r_v$ FAA	−55.83	−55.82	−55.81	−55.80
VDD FAA	−55.51	−55.25	−55.02	−54.72
VDD				
(ref. 15a)	—	−54.64	−54.40	−54.08
Exact <sup>a</sup>	—	−54.58	−54.30	−53.78

<sup>a</sup>Three-dimensional stabilized variational method.<sup>4a</sup>

The VDD approximation provides good agreement with the reference values demonstrating again the validity of rotational decoupling for the Ne  $\cdots$  Cl<sub>2</sub> complex. Comparison with the VDD/VRCC lifetime at  $v = 11$  (100 ps) reveals its overall accuracy, while the difference between our lifetime (112 ps) and the literature lifetime<sup>15b</sup> (116 ps) RIOSA- $J$  represents pure contribution of the FA approximation. The RIOSA- $I$  and  $-I'$  schemes again reproduce the reference data very well, whereas other parameterizations behave worse. As in the previous test, the RIOSA- $I_{\text{av}}$  option appears to be incompatible with FAA.

### He $\cdots$ ICl

The model used by Waterland et al.<sup>16</sup> for VP of the He  $\cdots$  ICl( $B$ ) complex served us as the third example. In that article decay dynamics of  $v = 2$ ,  $n = 0$  resonance were analyzed within the VDD/VDD RCC approach.<sup>16</sup>

**TABLE IV.**  
Lifetimes of the Ne  $\cdots$  Cl<sub>2</sub> Complex (Model II), ps.

Method	$v = 6$	$v = 9$	$v = 11$	$v = 13$
VDA- $r_e$ FAA / RIOSA- $I$	2370	513	202	86
/ RIOSA- $I'$	1888	425	170	73
VDA- $r_v$ FAA / RIOSA- $I$	1354	230	74	24
/ RIOSA- $I'$	1059	184	60	20
VDD FAA / RIOSA- $I$	1570	291	99	35
/ RIOSA- $I'$	1241	234	81	29
VDD / RIOSA- $J$				
(ref. 15b)	—	—	116	—
VDD / VRCC				
(ref. 15a)	1500	295	100	34
Wave packet (ref. 4a)	—	310	120	40

**TABLE V.**  
**Bending Levels of the He ... ICI Complex, cm<sup>-1</sup>.**

$n_b$	VDA- $r_e$ FAA		VDA- $r_v$ FAA		VDD FAA		VDD <sup>16</sup>
	$E, \text{cm}^{-1}$	$\delta, \%$ <sup>a</sup>	$E, \text{cm}^{-1}$	$\delta, \%$ <sup>a</sup>	$E, \text{cm}^{-1}$	$\delta, \%$ <sup>a</sup>	$E, \text{cm}^{-1}$
0	-13.905	-4.3	-13.869	-4.0	-13.895	-4.2	-13.331
1	-8.390	-8.4	-8.294	-7.2	-8.370	-8.2	-7.738
2	-6.536	-3.8	-6.482	-2.9	-6.518	-3.6	-6.294
3	-5.351	-2.6	-5.341	-2.4	-5.335	-2.3	-5.215
4	-3.505	+5.9	-3.550	+4.7	-3.502	+6.0	-3.725
5	-1.044	+30.6	-1.165	+22.5	-1.055	+29.9	-1.504

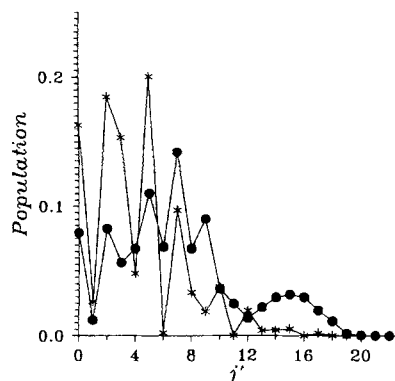
<sup>a</sup>Relative error with respect to VDD results (last column).

Table V lists energies of the van der Waals bending levels  $n_b$  associated with the ground stretching state  $n_s = 0$ . Comparison of VDD FAA estimations with the variational data from ref. 16 indicates that fixed angle approximation does not provide a uniform description of the bending spectrum: Giving an acceptable result for the ground state, it works even better for the center of bending manifold and gives rise to remarkable errors in energy of the highest states. This trend, also peculiar for other FAA variants, reflects the incorrect anisotropy of the effective angular potential  $W_{n_s}(\vartheta)$  [eq. (15)], which underestimates the energy of lower levels and pushes out the higher ones.

The data for lifetimes and product rotational energies are collected in Table VI. They illustrate the validity of rotational decoupling approximation for the He ... ICI system and completely confirm superiority of the RIOSA- $l$  and - $l'$  parameterizations. At the same time, for rotational product state distributions the RIOS approximation works slightly worse than in the case of symmetric vdW complexes (see Fig. 2).

**TABLE VI.**  
**Lifetimes and Averaged Product Rotational Energies for the Vibrational Predissociation of the He ... ICI Complex.**

Method	Lifetime (ps)	$E_{\text{rot}}(v' = 1), \text{cm}^{-1}$
VDD FAA / RIOSA- $J$	2564	1.56
/ RIOSA- $l$	2454	1.57
/ RIOSA- $l'$	1984	2.56
/ RIOSA- $l'_{\text{av}}$	1903	2.22
VDD / VDD RCC <sup>16</sup>	2180	6.31

**FIGURE 2.** Rotational distributions of dissociation products of the He ... ICI ( $B, v = 2$ ) complex: filled circles — VDD / VDD RCC,<sup>16</sup> stars — VDD FAA / RIOSA- $l'$ .

### Ne ... ICI

The last system considered here is the Ne ... ICI complex studied within the photodissociation theory,<sup>3b</sup> Fermi Golden Rule (VDD/VRCC and VDD/VDD RIOSA) approximation,<sup>3b,3c</sup> and time-dependent wave packet approach.<sup>4b</sup> The literature data together with our diabatically decoupled results are presented in Table VII for  $v = 2, n = 0$  and  $v = 2, n = 1$  resonances. The first evidence following from Table VII is the failure of FA approximation for the bound state wave function. Providing satisfactory resonance positions (2% error is even better than those pertinent to the other test systems), it overestimates lifetimes more than by an order of magnitude and predicts a qualitatively incorrect decrease in the lifetime of the bending-excited resonance  $n = 1$ . The use of variational bound state wave functions drastically improves agreement with the more accurate ap-



**TABLE VII.**  
**Energy, Lifetime, and Product Rotational Energy for the  $v = 2$ ,  $n = 0$  and  $v = 2$ ,  $n = 1$  Resonances of the**  
**Ne  $\cdots$  ICI Complex.**

Method	Energy ( $\text{cm}^{-1}$ )	Lifetime (ps)	$\langle E_{\text{rot}} \rangle^a$ , $\text{cm}^{-1}$
Ground state, $n = 0$			
VDD FAA / RIOSA-/	-43.047	32782	5.0
/RIOSA-/'		23006	9.5
VDD / RIOSA-/	-42.319	2763	3.8
/RIOSA-/'		2390	6.5
VDD / RIOSA-J <sup>3c</sup>	-42.3613	2678	—
/VRCC <sup>3b</sup>		2586	28.0
Lineshape <sup>3b</sup>	-42.3647	2504	27.6
Wave packet <sup>4b</sup>	-42.34	2600	—
First excited state, $n = 1$ ( $n_s = 0$ , $n_b = 1$ )			
VDD FAA / RIOSA-/	-35.118	16746	2.5
/RIOSA-/'		14236	17.6
VDD / RIOSA-/	-34.757	5422	14.2
/RIOSA-/'		4097	19.5
VDD / VRCC <sup>3b</sup>	-34.8464	3210	—
Lineshape <sup>4b</sup>	-34.8658	3110	—

<sup>a</sup>Averaged rotational energy in the  $v' = 1$  channel.

proaches, although a remarkable error still remains for  $n = 1$ . As for the rest, the picture observed for Ne  $\cdots$  ICI is consistent with that found for the other reference systems.

## Discussion

### VIBRATIONAL DECOUPLING APPROXIMATIONS

For two-dimensional models of a complex with frozen bending motion, the adiabatic decoupling crucially fails, underestimating predissociation rates by orders of magnitude.<sup>11b</sup> This effect, which is caused by mutual orthogonality of the initial bound state and final scattering wavefunctions determined with the same zero-order Hamiltonian, is certainly smoothed in the three-dimensional theory upon integration over the angle of orientation. Thus, one observes expected relative improvements of the results for both resonance positions and widths along the VDA- $r_e$ , VDA- $r_v$ , and VDD sequence. At the same time, the VDA schemes introduce remarkable (negative) error in energy, which may to some extent cancel the error related to wave functions in the Golden Rule integral [eq. (23)]. Further, the validity of adiabatic decoupling approximation depends on the excitation energy,

as one can see from the Ne  $\cdots$  Cl<sub>2</sub> (model II) data: As shown in Tables III and IV, deviation of the VDA results from the reference ones grows up with  $v$ .

Hence, the diabatic decoupling approximation is by far more appropriate for practical implementations despite additional computational expenses wasted for potential averaging [eq. (12)]. It provides not only more accurate lifetime estimations, but also predicts the correct dependence of the resonance position on the excitation energy. This opens a possibility to involve experimental information on the complex lineshifts in the potential inversion procedures.<sup>17</sup>

### FIXED ANGLE APPROXIMATION

The diabatic decoupling of the stretching and bending vdW vibrations of a complex—the FA approximation [eq. (14)]—relies on the difference in corresponding time scales. In other words, to satisfy the diabatic condition, one should require the bending frequency  $\omega_b$  to be much smaller than the stretching one  $\omega_s$ .

For all systems studied in this article, the ratio  $\omega_s/\omega_b$  ( $\omega_s$  and  $\omega_b$  are taken as the energy differences between the ground and first stretching and bending excited levels, respectively) is ca. 2.5, whereas the relative error of FAA for the ground

state energy varies from 2 to 7%. In agreement with Bratsev's theorem,<sup>18</sup> the FA approximation in all cases underestimates the exact (variational) energy for the ground state. The calculation on the He...ICl bending spectrum (Table V) demonstrates the lack of such strict correspondence for excited levels. This is confirmed by the absence of general relations between the exact and decoupled results for excited vibrational states.<sup>19</sup>

Providing an acceptable accuracy for resonance positions of all our test systems, the FA approximation may fail for widths. Indeed, Table VII unambiguously shows that the FAA introduces the order-of-magnitude error in lifetimes of the Ne...ICl complex, though it is valid for other systems.

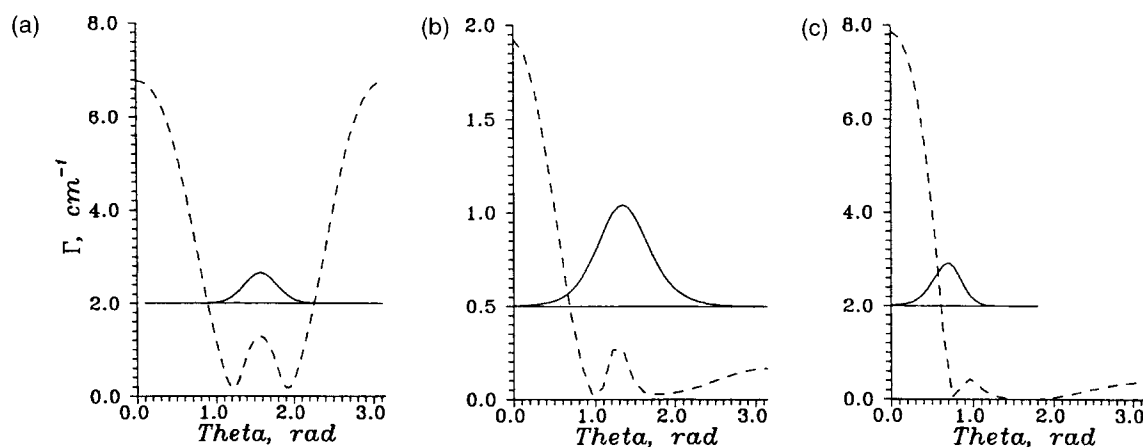
To rationalize this exception, the conditions for the FAA validity should be reformulated for the widths. Appealing to considerations relevant to the analysis of RIOSA in the vibration rotationally inelastic collision theory,<sup>20</sup> one must also take into account the time scale at which perturbation responsible for vibrational transitions varies with the orientation angle. In the present context, the angular dependence of the discrete-continuum matrix element of  $V$  should be inspected. Since it is difficult to quantify such analysis, we restrict ourselves to the qualitative illustration provided by Figure 3. Depicted are

$$\Gamma(\vartheta) = 2\pi \sum_{v'j'} \left| \langle \chi_{v'}(r) \phi_{\varepsilon v'j'}(R; \vartheta) \right. \\ \left. \times |V(r, R; \vartheta)| \chi_v(r) \phi_0(R; \vartheta) \rangle_{r, R} \right|^2$$

which are the values determined within the VDD FAA/RIOS approximation [see eqs. (8), (15), and (22)]. Angular wave functions  $F_0(\vartheta)$  [eq. (16)] are also shown (in an arbitrary amplitude scale). For the Ne...Cl<sub>2</sub> (model I) and He...ICl complexes, these functions are centered at  $\vartheta = \pi/2$  and cover the central maxima of  $\Gamma(\vartheta)$ . On the contrary, the Ne...ICl angular function is displaced toward the small angles, where the  $\Gamma(\vartheta)$  dependence exhibits a sharp minimum. Evidently, in the latter case integration over  $\vartheta$  should lower the vibrational transition probability, as observed numerically. Figure 3 indicates that the orientation behavior of the perturbation matrix element is more complex than the anisotropy of interaction potential, so it is unlikely that one could derive a general criterion for the applicability of fixed angle approximation for decay width. Nevertheless, as far as this approach provides an extremely simple and efficient computational scheme, one may follow here the advice of Kouri<sup>6</sup> concerning scattering RIOS approximation (i.e., "this approximation should be seriously considered even in cases where the validity conditions are not well satisfied").

### DECOUPLING OF THE PRODUCT SCATTERING CHANNELS

For all systems investigated here, the use of completely decoupled product scattering wave functions provides very good results for total vibrational predissociation rates. Failure of the decoupling approximation (primarily the vibrational one) should be expected only in the case of strong interaction among the asymptotic channels, which



**FIGURE 3.** Angular dependences of "width"  $\Gamma(\vartheta)$  (dashed line) and wave function (solid line) in the fixed angle approximation: (a) Ne...Cl<sub>2</sub> (model I); (b) He...ICl; (c) Ne...ICl.

usually manifests itself in a multiquantum intramolecular vibrational relaxation (IVR) assisted predissociation regime.<sup>3d, 17</sup>

On the other hand, single-channel scattering approximation is not able to reproduce sharing of the total width among product states. The VDD RIOSA scheme strongly overcools vibrational distributions and disturbs the rotational ones, particularly for the asymmetric complexes (see Figs. 1 and 2).

Our results indicate that among the variety of the RIOSA parameterizations with correct total angular momentum, the RIOSA-*l* and RIOSA-*l'* are the most accurate for lifetimes. The latter more correctly treats the energy distribution among the product states and therefore somewhat improves rotational distributions.

## Conclusions

Vibrational and rotational decoupling approximations for the bound state and scattering wave functions were tested in Fermi Golden Rule calculations on vibrational predissociation of the Ne...Cl<sub>2</sub>, He...ICl, and Ne...ICl van der Waals complexes. It was found that for these systems decaying via a direct mechanism (one-quantum vibrational transition), almost all schemes for separation of intramolecular and angular motions work qualitatively well. In particular, the following conclusions are in order:

1. Diabatic vibrational decoupling approximation is superior to the adiabatic one, providing correct dependence of the resonance position and width on excitation energy.
2. Fixed angle approximation for a quasibound vdW wave function gives good lower estimations for ground state energies, but its accuracy lowers for bending-excited resonances. It also works well in width calculations, although it may eventually fail for asymmetric complexes due to strong anisotropy of the perturbation matrix element.
3. Complete decoupling of scattering channels does not crucially affect lifetimes of the complexes under study but disturbs the product state distributions.
4. Rotational infinite order sudden approximation for scattering wave function should be parameterized according to total angular momentum of the complex *J*. The most appropriate schemes are RIOSA-*l* and RIOSA-*l'*.

5. The numerical radial functions generated for a system in a finite box as combined with angular functions of the fixed angle approximation form an effective basis set for variational calculations of the whole vdW spectrum.

## Acknowledgments

We thank Drs. E. A. Pazyuk, T. Yu. Mikhailova, and A. V. Stolyarov for valuable assistance and stimulating discussions. A. A. B. is also indebted to Profs. P. Villarreal and G. Delgado-Barrio for useful comments and hospitality during his stay at IFFAM (C.S.I.C., Madrid) arranged as a preliminary stage of the collaboration under the INTAS Program (INTAS 93-1809). Financial support from the Russian Fund of Fundamental Research under grants 93-03-04329 and 95-03-09710 is gratefully acknowledged.

## References

1. (a) D. H. Levy, *Adv. Chem. Phys.*, **47**, 323 (1981); (b) K. C. Janda, *Adv. Chem. Phys.*, **60**, 201 (1985); (c) G. Delgado-Barrio and J. A. Beswick, In *Floppy Molecules*, Y. G. Smeyers, Ed., Kluwer, Dordrecht, 1994, p. 203.
2. (a) *Structure and Dynamics of Weakly Bonded Molecular Complexes*, A. Weber, Ed., NATO ASI Ser. C, vol. 212, Reidel, Dordrecht, 1987; (b) *Dynamics of Polyatomic van der Waals Complexes*, N. Halberstadt and K. C. Janda, Eds., NATO ASI Ser. B, vol. 227, Plenum Press, New York, 1990.
3. (a) N. Halberstadt, J. A. Beswick, and K. C. Janda, *J. Chem. Phys.*, **87**, 3966 (1987); (b) O. Roncero, J. A. Beswick, N. Halberstadt, P. Villarreal, and G. Delgado-Barrio, *J. Chem. Phys.*, **92**, 3348 (1990) (c) O. Roncero, J. A. Beswick, N. Halberstadt, P. Villarreal, and G. Delgado-Barrio, *Bull. Soc. Roy. Soc. Liege*, **58**, 227 (1989); (d) N. Halberstadt, J. A. Beswick, O. Roncero, and K. C. Janda, *J. Chem. Phys.*, **96**, 2404 (1992).
4. (a) S. K. Gray and C. E. Wozny, *J. Chem. Phys.*, **91**, 7671 (1989); (b) S. K. Gray and C. E. Wozny, *J. Chem. Phys.*, **94**, 2817 (1991); (c) S. K. Gray, *Chem. Phys. Lett.*, **197**, 86 (1992).
5. (a) G. Delgado-Barrio, J. Campos-Martinez, S. Miret-Artes, and P. Villarreal, In *Dynamics of Polyatomic van der Waals Complexes*, N. Halberstadt and K. C. Janda, Eds., NATO ASI Ser. B, vol. 227, Plenum Press, New York, 1990, p. 409; (b) L. Beneventi, P. Casavecchia, G. G. Volpi, C. R. Bieler, and K. C. Janda, *J. Chem. Phys.*, **98**, 178 (1991).
6. D. J. Kouri, In *Atom-Molecule Collision Theory*, R. B. Bernstein, Ed., Plenum Press, New York, 1979, p. 301.
7. (a) E. Fermi, *Notes on Quantum Mechanics*, University of Chicago, Chicago, 1960; (b) A. Bohm, *Quantum Mechanics: Foundations and Applications*, Springer, New York, 1986.
8. M. Aguado, P. Villarreal, G. Delgado-Barrio, P. Mareca, and J. A. Beswick, *Chem. Phys. Lett.*, **102**, 227 (1983).

9. (a) J. A. Beswick and G. Delgado-Barrio, *J. Chem. Phys.*, **73**, 3653 (1980); (b) P. Villarreal, G. Delgado-Barrio, J. Campos-Martinez, and O. Roncero, *J. Mol. Struct. (THEOCHEM)*, **166**, 325 (1988).
10. D. E. Fitz, *Chem. Phys. Lett.*, **55**, 202 (1978).
11. (a) R. J. Le Roy, M. R. Davis, and M. E. Lam, *J. Chem. Phys.*, **95**, 2167 (1991); A. A. Buchachenko, A. Yu. Baisogolov, and N. F. Stepanov, *Russ. J. Phys. Chem.*, **68**, 660 (1994) (in Russian).
12. (a) J. E. Grabenstetter and R. J. Le Roy, *Chem. Phys.*, **42**, 41 (1979); (b) G. Brocks, *Mol. Phys.*, **62**, 1483 (1987).
13. (a) A. V. Abarenov and A. V. Stolyarov, *J. Phys. B*, **23**, 2419 (1990); (b) A. V. Stolyarov, *Spectrosc. Lett.*, **25**, 271 (1992).
14. D. D. Evard, F. Thommen, J. I. Cline, and K. C. Janda, *J. Phys. Chem.*, **91**, 2508 (1987).
15. (a) J. I. Cline, N. Sivakumar, D. D. Evard, C. R. Bieler, B. P. Reid, and K. C. Janda, *J. Chem. Phys.*, **90**, 2605 (1989); (b) N. Halberstadt, O. Roncero, and J. A. Beswick, *Chem. Phys.*, **129**, 83 (1989).
16. R. L. Waterland, M. I. Lester, and N. Halberstadt, *J. Chem. Phys.*, **92**, 4261 (1990).
17. A. A. Buchachenko, A. Yu. Baisogolov, and N. F. Stepanov, *J. Chem. Soc., Faraday Trans.*, **90**, 3229 (1994).
18. V. F. Bratsev, *Dokl. AN SSSR (Proc. Ac. Sci. USSR)*, **160**, 570 (1960) (in Russian).
19. T. Yu. Mikhailova, V. B. Pavlov-Verevkin, and V. I. Pupyshchev, *Vest. Mosk. Univ., Ser. Khim. (Bull. Mosc. Univ., Ser. Chem.)*, **31**, 7 (1990) (in Russian).
20. E. E. Nikitin, *Elementary Energy Transfer Processes in the Triatomic Systems*, VINITI, Moscow, 1985 (in Russian).